A Study of the Vapor Pressures of Certain Hydrated Metallic Sulphates

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DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
FACULTY OF PURE SCIENCE, COLUMBIA UNIVERSITY

BY

Eric Randolph Jette, B.S., M.A.

NEW YORK CITY
1922

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Dedicated to my parents

ACKNOWLEDGMENT

It is with pleasure that the author acknowledges his indebtedness to Professor C. D. Carpenter for his constructive criticism and generous coöperation during the progress of this investigation.

CONTENTS

SUBJECT MATTER

	Page
Abstract of the Dissertation	6
Introduction	7
The Static Method and Difficulties in its Use	8
The Use of the Static Method by Various Investigators	11
Description of Apparatus	12
Experimental Procedure	15
Discussion of the Accuracy of the Results	18
Interpretation of the Results	20
Application of the Results	21
Summary	25
Vita	27

ILLUSTRATIONS

Fig. 0.	Typical Static Instruments	9
Fig. 1.	Thermostat for Higher Temperature	13
Fig. 2.	Tensimeter Used in the Investigation	14
Fig. 3.	Rate of Approach to Equilibrium	16
Fig. 4.	Curves for Vapor Pressure Data	18
Fig. 5.	Solubility Curves for $MgSO_4$ and $CdSO_4$	20
Fig. 6.	Log $p - \frac{1}{T}$ lines	24

ABSTRACT OF DISSERTATION

1. What was attempted.

An attempt was made to measure the vapor pressure of certain hydrated salts at several points over a considerable range of temperature in order to study the phenomenon as a function of the temperature.

2. What were the methods?

(*a*) Special emphasis was placed upon the construction of a thermostat to operate at the higher temperatures.

(*b*) Improvements in the technique in the use of the tensimeter were employed.

(*c*) Equilibrium was approached from higher and lower pressures.

3. In how far were the attempts successful?

Considerable data has been obtained on six hydrates, and on the saturated solution of some of them above the transition point. The experimental errors usually encountered in determining vapor pressures have been practically eliminated.

4. What contributions actually new to the science of chemistry have been made?

(*a*) The collection of complete vapor pressure data for several hydrates and saturated solutions has been accomplished.

(*b*) Certain new transition points have been located by this method:

$$CoSO_4(7H_2O\text{–}6H_2O) \text{ at } 45.1^\circ \text{ C}$$

$$CdSO_4(\tfrac{8}{3}H_2O\text{–}1H_2O) \text{ at } 41.5^\circ \text{ C.}$$

The transition point of

$$MgSO_4(7H_2O\text{–}6H_2O) \text{ at } 48.4^\circ \text{ C}$$

previously found by Van der Heide between 48° and 48.5° has been verified.

(*c*) It has been shown that the vapor pressures of the hydrates and saturated solutions investigated may be expressed as a continuous function of $\log p$ and $\frac{1}{T}$, in the same manner as the vapor pressure of water and of solutions of various concentrations.

(*d*) The results have been calculated for the Heat of Vaporization.

A STUDY OF THE VAPOR PRESSURES OF CERTAIN HYDRATED METALLIC SULPHATES

Introduction

That many substances are volatile or decompose to give one or more gases, and that the tendency to do so is a definite function of the nature of the substance and the conditions imposed upon them, and that this tendency is measurable in terms of the pressure of the gas phase (usually called the vapor pressure of the system) is well known. The tendency for certain salt hydrates to gain or lose water is cited in the early literature of chemistry. Vogel[1] in 1818 reports that blue vitriol effloresces rapidly over sulphuric acid or fused calcium chloride, and little or not at all in the air. In 1838 Watson[2] made what seems to be among the first attempts to measure quantitatively the tendency for a salt hydrate (sodium carbonate) to effloresce, and expressed his observations in terms of the humidity of the air in which efflorescence begins. Mitscherlich[3] describes the measurement of the lowering of the mercury column in a "Torecelli Barometer" when a crystal of sodium sulphate is introduced into the free space above the mercury.

Wilson[4] has recently pointed out that the work on the vapor pressure of salt hydrates "prior to 1875 had little scientific value owing chiefly to the hazy notions which prevailed as to the nature of the phenomenon." Although Gibbs[5] formulated the phase rule in 1877, it was nearly fifteen years later before its merits were recognized. It seems, however, that during this period several investigators of the vapor pressure of salt hydrates recognized the necessity of the presence of two solid phases in order to define the point of equilibrium, and as shown by the nature of their results, real progress may be said to date from this period. An understanding of the phenomenon resulted in the development of new methods for measuring the vapor pressure at the point of equilibrium.

Although numerous investigators have studied the vapor pressure of salt hydrates as a function of the temperature, the data is still very incomplete. Much of the work has been done in order to test the method proposed, or as Wilson[6] points out, "for the express purpose of substantiating van't Hoff's equation and other thermodynamic laws for the case of salt hydrates," rather than to collect extensive data on a single hydrate. It was therefore only necessary to obtain a result at one or two temperatures. The temperatures usually chosen were 25° C or the boiling-point

[1] *Schweigger's Journal*, **22**, 160 (1818).
[2] *J. Prakt. Chem.*, **14**, 112 (1838).
[3] *Lehrbuch Der Chemie*, 4th Edition.
[4] *J. Am. Chem. Soc.*, **42**, 704 (1921).
[5] *Trans. Connecticut Acad.*, 1874–1878.
[6] *Loc. cit.*

of some liquid, and in only a few cases were experiments carried out at other temperatures. Wiedemann[7] carried some measurements up to 98.5° C, Schottky[8] a few at 90° C, and Derby and Yngve[9] from 10° to 140° C.

Many methods for determining the vapor pressure of substances have been developed. Extensive experiments, comprehensive discussions and bibliographies of the more important investigations have been given by Johnson[10] on hydroxides and carbonates, by Smith and Menzies[11] on general methods as applied to all phases of the subject, by Menzies[12] on "Apparent Anomalies Outstanding in the Results of Measurements of Dissociation Pressures," and by Wilson[13] in a recent paper on "Some New Methods for the Determination of the Vapor Pressure of Salt Hydrates." It seems agreed that the methods can best be classed under three heads. (1) Static, (2) Dynamic, and (3) Indirect. We shall not attempt a general discussion of these methods as the discussions just cited seem adequate.

A careful consideration of the literature, which revealed the lack of experimental data on the vapor pressure of salt hydrates over a wide range of temperatures; the disagreement in the results of previous investigators; in most cases, failure to study the approach of equilibrium from both sides; the usual assumption that equilibrium is reached quickly; and many other conspicuous cases of oversight or error, made it seem worth while to make a careful experimental study of the vapor pressure of a few of these salt hydrates. Preliminary experiments with certain hydrated sulphates demonstrated that the equilibrium is reached slowly, especially at the lower temperatures at which most previous investigators worked. It was therefore decided that some form of the static method would best serve our purpose, as when once set up, it might be used indefinitely. In order that our method and apparatus may be better understood, we shall briefly discuss "The Static Method where a Confining Liquid is Employed" and the "Difficulties Encountered," and "The Use of the Static Method by Previous Investigators."

The Static Method Where a Confining Liquid is Employed and the Difficulties Encountered in its Use

Types of Apparatus.—An idea of the general nature of the different types of apparatus designed for vapor pressure measurements, by means of a confining liquid, may be most easily understood by noting the sketches in Fig. 0. In (*a*) the substance is introduced into the free space above the

[7] *Wied. Ann.*, **17,** 561 (1882).
[8] *Zeit. physik. Chem.*, **64,** 415 (1908).
[9] *J. Am. Chem. Soc.*, **38,** 1439 (1916).
[10] *Zeit. physik. Chem.*, **62,** 330 (1908).
[11] *J. Am. Chem. Soc.*, **32,** 907; **32,** 1412; **32,** 1434; **32,** 1449, and **32,** 1541 (1910).
[12] *J. Am. Chem. Soc.*, **42,** 1915 (1920).
[13] *Loc. cit.*

mercury column in a Torecelli Barometer and the vapor pressure is read directly by the lowering of the column of mercury. In (*b*) the substance is introduced into the shorter arm of a J tube, and the confining liquid into the U. Both arms are then evacuated and sealed off. The pressure is then read directly in terms of the difference in the height of the liquid columns in the U. In (*c*) the substance is introduced into the bulb on the left and after adding mercury as confining liquid, the bulb is evacuated and sealed off. The pressure is determined by noting the height of the columns and adding or subtracting as the case may require the difference from the barometer reading. In (*d*) the substance is placed in the bulb on the left

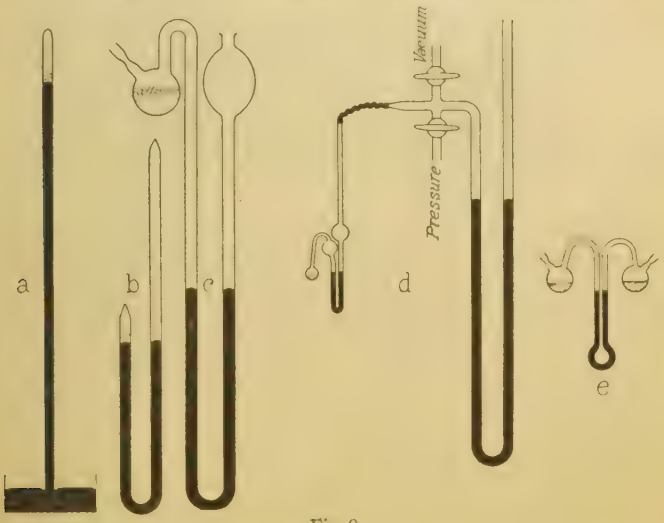

Fig. 0.

and the confining liquid into the U. The open end of the instrument is then attached to a vacuum pump, tilted on one side and evacuated. It is then brought to an upright position so the free spaces in the two arms are separated by the confining liquid. In order to make readings, the open end must be connected to a manometer, and vacuum and pressure pumps so that the pressure in the open arm can be made equal to that of the vapor pressure of the substance. When the columns are at the same height, the manometer gives the pressure exerted by the gas liberated from the substance. In (*d*) the substance is placed in one bulb, the confining liquid into the U, and a reference substance, the vapor pressure of which is known, in the other. Both bulbs are simultaneously evacuated and sealed off while keeping the instrument in an upright position. The pressure is then determined by adding to or subtracting from the difference in the height of

the columns of the confining liquid, the known pressure of the reference substances, depending on whether its vapor pressure is greater or less than that of the reference substance. Many modifications of the types illustrated have been used, but those described above embody the general principles employed in all. Those who have used any one of these types, selected it because it could be used to better advantage in the problems under consideration. The difficulties which are encountered in these types and the various modifications are about the same and some of the most conspicuous are considered below.

Enclosed Gas.—One of the chief errors in the static method may result from gas which is not entirely eliminated when the instrument and its charge is prepared for use. Among the most conspicuous sources of gas in such an instrument are (*a*) upon the walls of instrument, (*b*) upon the surface of the material in the instrument, absorbed or adsorbed, (*c*) occluded mechanically in pockets in the substance, and (*d*) dissolved in the crystal or inclosing liquid. In case a differential method is used, the same troubles with gas may arise on the side in which the reference substance is contained.

Manometer Liquid.—The nature of the manometer liquid may be such as to introduce considerable error. An ideal manometer liquid would be one that is light in order that small changes in the pressure can be easily recognized; has no vapor pressure so that the gas pressure represents only that of the substance under investigation as well as to prevent its distillation and subsequent contamination of the substance; is non-solvent for the gases in order to prevent transmission of gases from one side of the instrument to the other; and one which does not "wet" the instrument as such a meniscus is easier to read when the height of the liquid column is being noted.

Obtaining Equilibrium.—The difficulties in obtaining equilibrium have not been as seriously considered by some investigators as they should have been. One of the difficulties, that of maintaining a constant temperature, has been extensively studied and met by the design of very efficient thermostats adjustable to any temperature up to about 50° C. A second difficulty arises in the choice of the static method. If equilibrium is reached immediately, an isotenoscope of the Smith and Menzies[14] type may be used, but in case the equilibrium is reached slowly, it could only be used by inclosing the manometer in the thermostat, *i. e.*, if readings in fractions of mm. of mercury were desired. As shown in Fig. 0 (*d*) the isotenoscope is introduced into the thermostat, and its open end is attached through tubing to a vacuum bottle, pump, and manometer, so that the confining liquid may be leveled at (*a*) making the pressure equal on both sides. Any change in the room temperature would be registered by a

[14] *J. Am. Chem. Soc.*, **32**, 1413, Fig. 3 (1910).

change of level in the confining liquid. Since a manometer standing in a room undergoes the same temperature change as the room, a variation of 1° C in a room at 20° C changes the pressure 2.5 mm. on a system registering 760 mm. This would result in a corresponding change in height of the columns of the confining liquid. In case a light liquid were used, a much greater difference in the height of the leveling liquid would result. If the equilibrium is reached slowly, a change in the temperature of the room would therefore impose an excessive pressure at one time and a diminished pressure at another. In fact, as true equilibrium is approached, the reaction would be forced backward at one time and forward at another, and any reading taken could be correct only accidentally. It is therefore evident that a method for use in case of a slow approach to equilibrium must be one in which no manipulation will effect a change in conditions during the progress of the reaction.

The Use of the Static Method by Various Investigators

The Bremer-Frowein Tensimeter. Frowein[16] in studying the vapor pressure of certain hydrated salts used a differential method, illustrated in Fig. 0 (c) similar to one previously used by Bremer. This instrument is known as a Bremer-Frowein Tensimeter. Frowein used olive oil as enclosing liquid with concentrated sulphuric acid on one side to produce a zero pressure of water vapor on that side. His results have been much quoted and in spite of certain difficulties not overcome by him, the work is of considerable value. Andreae[17] used the tensimeter, with oil as the confining liquid, to study the equilibrium of a hydrate when containing different amounts of the same two solid phases, by balancing one against another. As a result of his experiments, he discovered that there were limits between which the compositions of the solid phase might vary, but over which no difference in vapor pressure could be recognized. Although the phase rule was not known to him, the conclusions given by him coincide with those required by its application. Schottky[17] used the tensimeter with paraffin oil as confining liquid to study the approach of equilibrium when reached from both sides, by putting the same hydrate in both bulbs and heating one to a higher temperature than that at which the approach to equilibrium was to be studied, but was unable to satisfactorily account for some of the difficulties. Cohen[18] used the tensimeter with mercury as confining liquid when studying vapor pressures of hydrates, and applied his data to a calculation of the heat of hydration. Menzies[19] investigated the so called "anomalies" of other investigators, in some cases

[16] *Zeit. physik. Chem.*, I, 5 (1887).
[17] *Zeit. physik. Chem.*, **7**, 241 (1891).
[17] *Loc. cit.*
[18] *Zeit. physik. Chem.*, **36**, 517 (1901).
[19] *Loc. cit.*

repeating their work and concludes that "the real facts exhibit no anomalies." This work included the use of the tensimeter in testing some of Frowein's results and gives reasons "for accepting the tensimetric results of Frowein, often regarded as standard, only with caution," and a possible explanation of some of Schottky's difficulties.

Open End Tensimeter Attached to a Manometer.—In measuring the vapor pressure of hydroxides and carbonates, Johnston[20] used a modification of the tensimeter, one arm of which was attached to a manometer standing in a room, and made his readings in mm. of mercury. He eliminated much of the error in his results for the hydroxides by plotting the observed temperature against the temperature of water at which it would have the observed pressure for the hydroxide in order to derive a formula with which he calculated the temperature at which the hydroxide should give the observed pressure. As the corrected temperatures varied, in some cases, 9° C from that of the observed, the errors due to change in temperature of the room and its effect upon the equilibrium as pointed out in our discussion above may be neglected. Derby and Ingve[21] used the isotenoscope method described by Smith and Menzies[22] for measuring the vapor pressures of certain salt hydrates. They emphasized that temperatures were accurately obtained and that they used a paraffin oil with negligible vapor pressure so that the record of change of pressure could be more readily recognized, but do not discuss the difficulty arising from the change of temperature in the room as we pointed out in the discussion above. It must be assumed that the salts used by them reached equilibrium before any change in the room temperature took place as they give results in fractions of mm. of mercury.

Only a few cases have been cited, but sufficient to give a general idea of the nature of the work already done along the lines which have been involved in this investigation. As already pointed out the articles cited have gone much more completely into certain other phases of the work done by various investigators.

Description of Apparatus

As this investigation has been carried out in order to obtain vapor pressures of certain hydrated sulphates at several temperatures by allowing equilibrium to be reached from both sides, thermostats which gave constant temperature control over long periods of time were required. The instrument by which the actual measurements were made was designed so that when once set up, it could be used at various temperatures and over a long period of time.

[20] *Loc. cit.*
[21] *Loc. cit.*
[22] *Loc. cit.*

The Thermostats.—Four thermostats have been used. A Freas thermostat Type 5132 (E and A catalogue) was used at 25° C and one of Type 5132 1 from 30° to 50° C. For temperatures from 50° to 65° C a Pyrex jar 9½″ × 15″ was insulated with "Magnesia" 1½″ thick and regulated by means of a Freas regulator. A narrow window was made in the insulation so that readings could be made. For temperatures from 65°

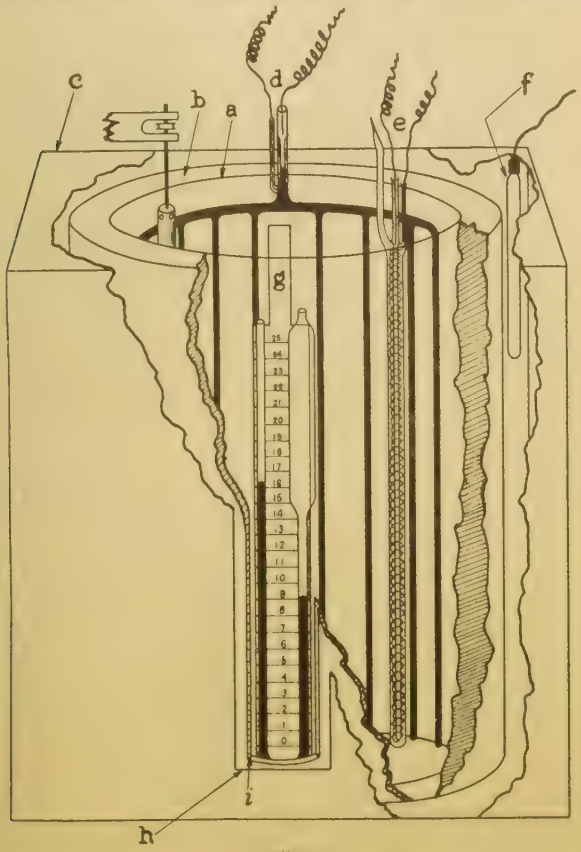

Fig. 1.

up and during the later experiments down to 60°, a special thermostat was assembled, Fig. 1. A Pyrex jar (*a*), referred to above, insulated with magnesia (*b*) was surrounded by an asbestos box 15″ × 15″ × 15″ (*c*) in which an electric bulb (*f*) of appropriate capacity could be suspended to keep the temperature very near that at which the thermostat was set.

This box had a small removable door (*h*) in front of the window (*i*) in the magnesia insulation, which could be opened when readings were to be taken. Water was put into the jar and covered with a $\frac{1}{2}$″ layer of paraffin. The whole thermostat, stirrer and other attachments were inclosed in a space surrounded and covered by a large wool fire blanket supported by four tall posts. This acted as a second chamber in which electric bulbs could be suspended to keep a constant temperature. The thermostat was thus kept in a double "constant temperature room."

The regulation of the temperature was accomplished by a thermoregulator, (*d*), mercury in glass, making and breaking an electric circuit by contact of the mercury in a capillary with a platinum point. In order that the regulator should register small temperature changes in all parts of the bath, it was constructed of $\frac{5}{8}$″ Pyrex tubing having eight fingers as shown in Fig. 1 (*d*). The electric circuit was attached to a controlling device, designed by D. and J. Beaver,[23] which opened or closed the intermittent electric heaters. These heaters (*e*) were made by sealing a coil of Driver Harris wire in an evacuated Pyrex glass tube 15″ long by $\frac{5}{8}$″ diameter. One was used as a continuous heater and one or two, as needed, as intermittent.

The stirring was accomplished by a turbine propeller in a tube 14″ × $1\frac{1}{2}$″ and mounted as described by Carpenter.[24] This produced a rapid circulation of the water in the bath.

The Tensimeter.—Fig. 2, A, illustrates the principle features of the tensimeter. It was of Pyrex tubing, 12″ over all, and except for the bulbs of heavy wall 4 mm. I. D. tubing. The tensimeter was mounted upon a support carrying a scale etched upon a strip of milk glass. This strip was 270 mm. long and 25 mm. wide and calibrated from 0, at 10 mm. from the lower end, to 250 mm. near the upper. The mounting is shown in Fig. 2 B.

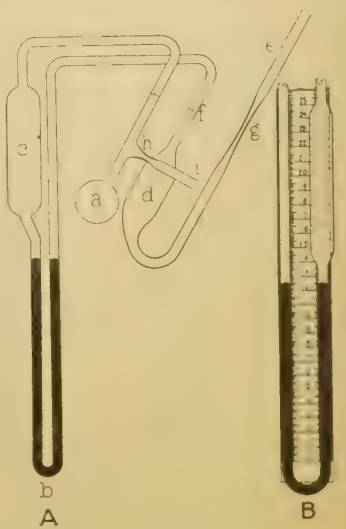

Fig. 2.

The Thermometer.—The thermometers were all mercury in glass and were calibrated every five degrees by a platinum resistance thermometer standardized as described by the Bureau of Standards.[25]

[23] Description to be published.

[24] *Chem. and Met. Eng.*, **24**, 569 (1921).

[25] Reprint 124; *J. Am. Chem. Soc.*, **41**, 748 (1919).

Experimental Procedure

Preparation of the Hydrates.—Chemically pure hydrates were dissolved in pure water and recrystallized five or six times. After each crystallization the solid was drained from the mother liquor and washed. The final crystallization was always carried out by evaporation of the water at low temperatures. The lower hydrate was obtained by gently heating the higher until sufficient water had been driven off. The water composition of the hydrates used was determined in all cases by analysis.

Preparation of the Tensimeter. The tensimeter was thoroughly washed with an alkaline solution, rinsed out and washed with sulphuric acid chromate "cleaning solution." It was then washed with pure water and finally steamed out.

Preparation of Mercury. The mercury used as enclosing liquid was washed with nitric acid as described by Hildebrand[26] and finally distilled under a partial vacuum with a slow steam of air bubbling through it.

Loading the Tensimeter. The mercury was introduced into the U and after bringing to a vertical position, conductivity water was distilled through the side arm (*i*) into the bulb (*a*). After about 2 cc. had been collected, the side arm was sealed off at (*h*). This then gave water essentially free from dissolved air except for the air in the tensimeter. The hydrate was then put into the bulb (*d*) which was then sealed on at (*f*). Experience showed that one of the main precautions necessary was involved in making the seals in the glass. In an extreme case which was encountered, there was a slow leak that during the course of three weeks amounted to 20 mm. of mercury pressure. An oxygen gas torch was therefore used, and all seals were gone over carefully.

The tensimeter was placed in a horizontal position so that the mercury was in bulb *c*, and attached at *e*, through pressure tubing, to a "Cenco" pump capable of producing a 1-mm. vacuum. The pump was then started and a vacuum of 2 or 3 mm. maintained for from 1 to 2 hours. During this period the tensimeter was alternately heated and cooled. When gently warmed the mercury boiled. All parts of the instrument except the bulbs containing the mercury and water were heated very hot during evacuation. The instrument was gently tapped to aid in the removal of any gas trapped by the water, mercury or hydrate. During the evacuation 0.3 to 0.5 cc. of water distilled off. Since 0.1 cc. of water vapor at 760 mm. pressure occupies about 160 cc., the tensimeter and surface of the hydrate was therefore washed with a stream of 150 to 250 liters of water vapor at 2 to 3 mm. pressure.

While the vacuum was maintained the tensimeter was brought to a vertical position, and after gently warming the hydrate until slight evidence of dehydration took place, it was sealed off at (*g*). From two to four

[26] *J. Am. Chem. Soc.*, **31**, 933 (1909).

tensimeters were loaded with the same hydrate. These were then mounted as shown in Figs 1g or 2B, so that they could be put into the thermostat or removed whenever desired. Some of these tubes were used for months.

Whenever measurements were to be made, 2 tensimeters were loaded with the same hydrate. One was then heated until the salt was partially dehydrated. After setting the thermostat, both tensimeters were introduced, one registering a lower pressure and one a higher pressure than

TABLE I

$CuSO_4 . 5H_2O$-$3H_2O$ AT 35.17°

Pressure in millimeters (corr.)

Date April	From lower H_2O pressure	From higher H_2O pressure	Date April	From lower H_2O pressure	From higher H_2O pressure
1	Started	Started	9	16.4	16.9
3	15.7	17.8	10	16.4	16.5
4	15.9	17.5	12	16.5	16.5
5	16.1	17.3	14	16.5	16.6
6	16.1	16.9	..	..	..
8	16.3	16.8	..	Mean final value, 16.5	..

they should at the point of equilibrium. This resulted in a slow increase in pressure in one case and a decrease in the other; thus equilibrium was approached from both a higher and a lower pressure at the same time.

Data on the determination of one point at 35.17° for $CuSO_4 . 5H_2O$-$3H_2O$ are given in Table I and graphically expressed in Fig. 3.

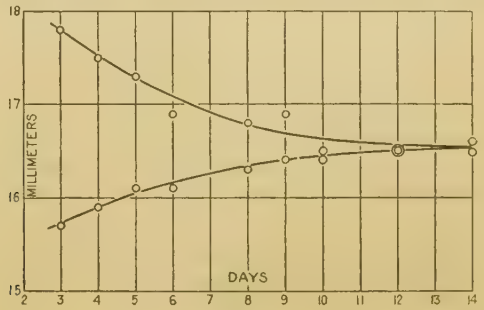

Fig. 3.

The vapor pressures were obtained in this manner at several temperatures for the hydrates $CuSO_4 . 5H_2O$–$3H_2O$, $CuSO_4 . 3H_2O$–$1H_2O$, $MgSO_4 . 7H_2O$–$6H_2O$, $CoSO_4 . 7H_2O$–$6H_2O$, $CdSO_4 . 8/3H_2O$–$1H_2O$, $MnSO_4 . 5H_2O$–$1H_2O$ and for the saturated solutions of $MgSO_4 . 6H_2O$, $CoSO_4 . 6H_2O$, $MnSO_4 . H_2O$. Table II gives in detail the actual readings and all calculations in obtaining the vapor pressures for the system $CuSO_4 . 5H_2O$–$3H_2O$,

and Table III shows the values for all other systems without the detailed readings and averaging as shown in Table II. The data of Tables II

TABLE II

THE VAPOR PRESSURE OF $CuSO_4.5H_2O$–$3H_2O$

Temp. °C.	Variation of thermostat ± °C.	Tensimeter No.	Diff. of Hg. levels corrected Mm.	Vapor press. H_2O Mm.	Variation in vapor press. of H_2O Thermostat ± Mm.	Vapor press. of hydrate Obs. Mm.	Mean Mm
25.00	0.004	5–4–6*	15.87–15.87–16.03	23.76	0.00	7.9–7.9–7.7	7.8
30.17	0.01	5–6*	20.8–20.4	32.15	0.02	11.4–11.8	11.6
35.13	0.01	5–6*	26.1–26.0	42.49	0.02	16.4–16.5	16.5
36.65	0.04	5–4*	27.7–27.9	46.18	0.10	18.5–18.5	18.5
40.12	0.04	5–4*	32.6–32.5	55.69	0.12	23.1–23.2	23.2
45.07	0.03	5–4*	39.4–39.5	72.16	0.12	32.8–32.7	32.8
50.16	0.03	5–4*	47.9–48.2	93.38	0.15	45.5–45.2	45.4
55.29	0.05	5–4*	58.1–57.9	119.8	0.29	61.7–61.9	61.8
60.18	0.05	5–4*	67.2–66.7	150.7	0.35	83.5–84.0	83.8
60.46	0.01	6–5*	67.0–67.2	152.7	0.07	85.7–85.5	85.6
65.16	0.04	5–4*	76.3–76.4	188.9	0.34	112.6–112.5	112.6
70.16	0.02	8*	85.0	235.4	0.21	150.4	150.4
69.78	0.02	6–5*	84.4–83.9	231.5	0.21	147.1–147.6	147.4
80.13	0.03	6–5*	96.9–97.7	357.4	0.45	260.5–259.7	260.1
90.04	0.03	8–9–8*	94.3–94.1–93.9	526.8	0.60	432.5–432.7–432.9	432.7

TABLE III

CONDENSED TABLE OF VAPOR PRESSURES DETERMINED AS INDICATED IN TABLE II FOR

t °C.	p	t °C.	p	t °C.	p
$CuSO_4.3H_2O$		$CdSO_4.8/3H_2O$		$CoSO_4.7H_2O$	
25.00	5.6	25.00	17.8	25.00	17.0
35.13	11.8	24.99	17.6	32.50	28.7
45.17	22.1	30.17	25.5	36.65	38.0
50.23	30.9	35.17	35.0	40.18	48.1
65.11	77.7	40.12	47.8	40.22	48.4
80.08	183.1	40.25	48.7	45.07	66.0
80.05	183.5	45.07	63.8	45.17	66.5
$MgSO_4.7H_2O$		45.17	64.7	50.16	84.9
25.00	12.7	50.16	84.5	55.29	107.7
32.40	22.8	50.23	84.0	60.22	134.9
36.65	31.4	55.29	110.2	65.16	167.3
36.65	31.5	60.22	140.0	70.16	204.3
40.12	40.1	65.16	175.7	$MnSO_4.H_2O$	
40.19	40.6	70.16	218.6	25.00	19.8
40.22	40.6	75.87	279.3	24.99	20.1
45.07	57.2	80.03	334.3	30.17	27.1
45.21	58.0	80.03	334.6	32.47	31.1
50.16	78.6	90.04	500.3	35.17	37.0
50.29	79.0	...	...	36.65	40.4
55.26	99.3	...	...	40.17	49.1
55.33	99.6	...	...	40.19	49.3
60.18	123.5	...	...	45.14	64.4
65.15	153.0	...	...	60.29	138.7
65.11	153.9	...	...	65.16	174.7
69.74	185.7	...	...	...	...

and III are expressed graphically in Fig. 4. Those marked with an asterisk are the tensimeters in which equilibrium was approached from the higher vapor pressure.

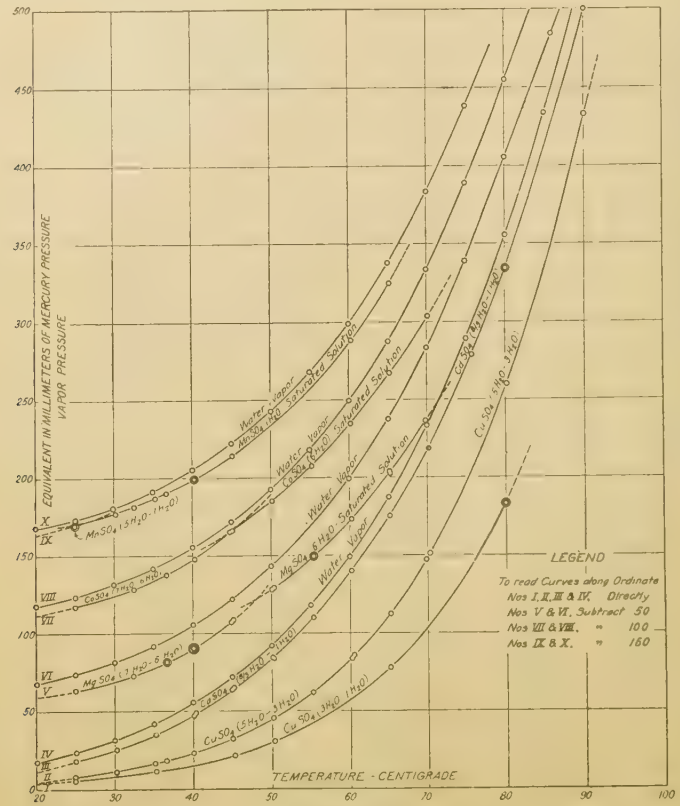

Fig. 4.

Discussion of the Accuracy of the Results

As this investigation was undertaken in order to obtain results with the greatest degree of accuracy, a brief review of the precautions taken in the experimental work and an estimation of the accuracy of the results obtained should be made. The preparation of pure hydrates and pure water have already been described. The necessity of knowing the exact temperatures was also recognized and a determination of them accomplished by standardizing the thermometers used, as described before. Enclosed "permanent gas," which is recognized as one of the chief difficulties,

was removed by warming and washing the surface of all materials and apparatus with a stream of water vapor at low pressures as described previously. That it was eliminated is evident from the fact that instruments set up at different times and containing different amounts of water, hydrate, mercury, and exposed glass surface, gave satisfactory duplication in results. A further evidence is the fact that the same instrument used over a long period of time and at many different temperatures gave duplicate results when brought back to the temperatures used in the earlier experiments. In fact, new instruments when set up duplicated the results of others that had been prepared months before. A further possibility of error results in the reading of the mercury columns and the regulation of the thermostat. The reading of the heights of the mercury columns could readily be made with an error of not more than ± 0.1 mm. and if this were $+0.1$ mm. in one reading and -0.1 mm. in the other, the error would be cumulative, or a total error of ± 0.2 mm. The variation in the temperature also leads to some error, as a change of $0.69°$ at $25°$ causes a change of 1 mm. in the vapor pressure of water, and $0.049°$ causes the same change at $90°$. At the lower temperatures the regulation was better than $0.005°$ and at the higher within $0.03°$. The maximum error due to variations in temperature of the thermostat would therefore be less than 0.01 mm. at $25°$ and about 0.6 mm. at $90°$.

Whether these apparent maximum errors are real is a pertinent question. At the lower temperatures, where equilibrium is reached slowly, an error of ± 0.6 mm. due to thermostat regulation would become very serious, but no such difficulty exists. On the other hand, at the higher temperatures equilibrium is reached quickly and as the temperature of the thermostat is taken at each reading, the pressure at that temperature is probably close to the equilibrium pressure. Since the temperatures and pressures recorded at these higher points are averages of several readings, the error is far below the apparent error. If, however, we accept the individual maximum apparent errors on one tube as ± 0.2 mm. at the lower temperatures and ± 0.6 mm. at the higher, the shape of the vapor-pressure curve will be very near the true shape and any result obtained by reading the curve would be within the experimental error. An error of ± 0.2 mm. on a single point at $25°$ on a value of 10 mm. represents a possible error of 4% while an error at $90°$ of ± 0.6 mm. on a value of 250 mm. represents an error of less than 0.5%. Accepting the maximum apparent errors, the relative error at the higher vapor pressure becomes very small; but a 4% error at the lower pressure, if real, would seriously affect the absolute values. It must be borne in mind, however, that every tensimeter was read many times, and the average reading taken as the final, and that no point was determined by only 1 tube but by the average of at least 2. In order to make this 4% relative error real, every reading would need

to have a maximum error and always in the same direction, that is, it would always be necessary to read 1 tube consistently 0.2 mm. high and the other consistently 0.2 mm. low in order that each individual value should have a maximum error. That such an error could not be possible is better illustrated by considering the method of determining the point of equilibrium and the procedure in reading the value already shown in Table I and Fig. 2, which shows that the maximum ± 0.2 mm. error exists for only 2 of the 18 points. It is evident, therefore, that the real error is much below the maximum possible error obtained when considering the extreme cases.

Interpretation of the Results

The most evident lessons from the results of this investigation can be learned by a study of the curves in Fig. 4. As shown in Fig. 4, Curves V, VII and IX, a transition takes place and in two cases is located by the intersection of two curves.

In the case of $MgSO_4.7H_2O$–$6H_2O$ (see Curve V) the hydrate is stable up to 48.4°. The upper segment is the vapor-pressure curve for a saturated solution of $MgSO_4.6H_2O$. This verifies the findings of Van der Heide[27] who showed by the dilatometer that the transition point is between 48° and 48.5°. The solubility data as collected by Seidell[28] gives an indication of this point (see Fig. 5). Too much cannot be expected from these solubility data, as the 14 points are taken from 12 observers. The position of this point is only approximately located by solubility data.

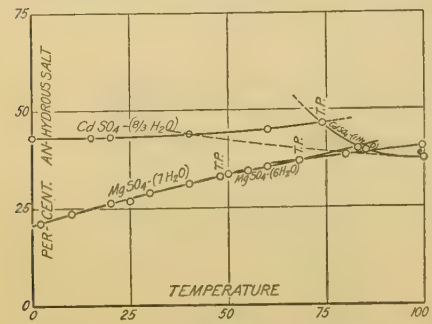

Fig. 5.

$CoSO_4.7H_2O$–$6H_2O$ is stable up to 45.1° (see Curve VII). No previous record of this point has been found. Marignac,[29] however, working with the dilatometer, found a transition point at 40.8° and by a thermometric method at 40.6°; our results show no indication of a transition of any kind around 40°.

The vapor-pressure curve for a saturated solution of $MnSO_4.H_2O$, and one point at 25° for the hydrate are given (see Curve IX). The hydrate is not stable above 27°. The transition point, therefore, cannot

[27] *Z. physik. Chem.*, **12**, 418 (1893).
[28] "Solubilities of Inorganic and Organic Substances," 2nd ed.
[29] *Assn. Chem. Phar.*, **97**, 247 (1856).

be located from our data by this method. The transition point has been found to be 27° by Cottrell.[30]

The vapor pressure of $CdSO_4.8/3H_2O$–$1H_2O$, determined over a wide range and plotted in Curve III, gives little evidence of any transition point. It must be noted, however, that the curve does not correspond with that of the water or with the other curves given. This might not be apparent at first, as it is "tangentially" parallel with the water curve but not parallel in the sense that a second curve is when measured by the distance along the ordinates. The peculiarity in vapor-pressure change seems to be paralleled by the peculiar change in solubility. Etard[31] found the greatest solubility to be at 68° while Mylias and Funk[32] found it to be between 73.5° and 74.5°, at which point the solubility commenced to drop very rapidly. If the solubility decreases as shown in the curve of Fig. 5, the solution grows rapidly more dilute above this point and thus results in causing the vapor pressure to increase more rapidly. It must be noted that the real change in solubility is small.

In the results for the vapor pressure of $CdSO_4.7H_2O$ given above, many points were duplicated several times and equilibrium was established very carefully. Although the shape of the curve gives little evidence of a transition point at 74°, it must be noted that it is peculiarly flat in this region. It will be shown below, however, that there are certain theoretical interpretations possible of its behavior.

Application of Results

Heat Reaction.—The heat reaction, which may in this case be considered as the latest heat of vaporization, has been calculated for each of the hydrates investigated except for that of manganese sulfate which was omitted for lack of data. In the reaction $AB.xH_2O + 1H_2O \rightleftarrows AB.(1+x)H_2O + Qp$, Qp is given by the following relation: $Qp = RT^2 \frac{d\ ln\ p}{d\ T}$. Qp is therefore the heat of reaction per mole of water at constant pressure; p is the pressure of water vapor of the system at equilibrium at the absolute temperature T. Since the value Q is very sensitive to changes in p and T, the extreme values may easily diverge $\pm 4\%$ from the mean value of Q for the system being considered. Q is determined for each system by substituting the experimental values recorded in Tables II and III in the formula, and are given in Table IV.

The average value for $CuSO_4.3H_2O$ is 13,256; for $CuSO_4.5H_2O$, 13,268; for $CdSO_4.8/3H_2O$, 11,170; for $MgSO_4.7H_2O$, 14,035; for $MgSO_4.6H_2O$, saturated solution, 9,741; for $CoSO_4.7H_2O$, 12,795; and for $CoSO_4.6H_2O$, saturated solution, 9,760.

[30] *J. Phys. Chem.*, **4**, 651 (1900).
[31] *Ann. chim. phys.*, [7] **2**, 536 (1894).
[32] *Ber.*, **30**, 824 (1897).

Values were also taken from the smooth curve III, Fig. 4, and used in making similar calculations and are given in the Appendix to Table IV. It may be observed that the calculated values for Q for the systems

TABLE IV

Temperature Interval	Qp Calories
$CuSO_4.3H_2O$–$1H_2O$	
25.00–35.13	13434
35.13–45.17	12183
45.17–50.23	13542
50.23–65.11	13469
65.11–80.07	13651
Average	13256
$CuSO_4.5H_2O$–$3H_2O$	
25.00–30.17	13789
30.17–35.13	13192
35.13–40.12	13100
40.12–45.17	13840
45.07–50.16	13051
50.16–55.29	12678
55.29–60.46	13713
60.46–65.16	12990
65.16–69.78	13401
69.78–80.13	13205
80.13–90.04	12993
Average	13268
$MgSO_4.7H_2O$–$6H_2O$	
25.00–32.40	14308
32.40–36.65	14299
36.65–40.19	13821
36.65–40.22	13706
40.19–45.21	14076
40.22–45.21	14163
45.21–48.42*	13871
Average	14035

* From curve

Temperature Interval	Qp Calories
$MgSO_4.6H_2O$–Saturated Solution	
48.42–50.29	9943
50.29–55.26	9708
50.29–55.33	9703
55.26–60.18	9633
55.33–60.18	9644
60.18–65.11	9996
65.11–69.74	9563
Average	9741
$CdSO_4\frac{8}{3}H_2O$–$1H_2O$	
24.99–30.17	12855
30.17–35.17	11763
35.17–40.25	12479
35.17–40.12	12078
40.25–45.17	11440
40.12–45.07	11521
45.17–50.23	10548
45.07–50.23	10895
50.23–55.29	11317
55.29–60.22	10557
60.22–65.16	10298
65.16–70.16	10077
70.16–80.03	10381
80.03–90.04	10247
$CoSO_4.7H_2O$–$6H_2O$	
25.00–32.50	12638
32.50–36.65	12719
36.65–40.18	12873
36.65–40.22	13066
40.18–45.07	12811
40.22–45.07	12664
Average	12795
$CoSO_4.6H_2O$-Saturated Solution	
45.17–50.16	10005
50.16–55.29	9779
55.29–60.22	9932
60.22–65.16	9761
65.16–70.16	9454

$CuSO_4.5H_2O$–$3H_2O$ and $CuSO_4.3H_2O$–$1H_2O$ vary on both sides of the mean value but no steady increase or decrease of value is indicated. It is note-

worthy that both systems show almost identical mean values for the calculated heat of vaporization over the same temperature range. In the case of $MgSO_4.7H_2O$-$6H_2O$, the calculated values of Q for the hydrate and the saturated solution are strikingly different. In fact this change is so evident that the approximate position of the transition point may be closely located. In order to appreciate this check on transition point, it must be borne in mind that the values used in the calculations were experimental.

In the case of $CoSO_4.7H_2O$–$6H_2O$, the same striking observations may be made as in the case of the $MgSO_4.7H_2O$–$6H_2O$ system.

In the case of $CdSO_4.8/3H_2O$–$1H_2O$, the calculated value of Q shows a fairly steady decrease up to about 70°, above which its value remains nearly constant. This is shown more clearly by the data given in the Appendix to Table IV which were calculated from values obtained by reading points at 5° intervals on the smooth curve in Fig. 4, Curve III.

TABLE IV APPENDIX

$$CdSO_4.\frac{8}{3}H_2O\text{–}1H_2O$$

Temperature Interval	Pressures from curve		Qp Calories
25.00–30.00	17.6	25.2	12886
30.00–35.00	25.2	34.8	11976
35.00–40.00	34.8	47.5	11924
40.00–45.00	47.5	63.6	11551
45.00–50.00	63.6	83.3	11019
50.00–55.00	83.3	108.7	11209
55.00–60.00	108.7	139.6	10552
60.00–65.00	138.6	174.2	10230
65.00–70.00	174.2	217.3	10189
70.00–75.87	217.3	279.2	10158
75.87–80.00	279.2	333.8	10587
80.00–90.04	333.8	500.3	10269

Relation between Temperature and Pressure.—Very few attempts to find a mathematical expression for the variation of pressure with temperature in the case of hydrates have been reported in the literature. This is probably due to the short temperature ranges covered by previous investigators and, therefore, insufficient data on the subject. Pareau,[23] however, noted that his curves were, in general, similar to that of pure water. Baxter and Lansing[24] plotted the logarithm of the aqueous pressure against the reciprocal of the absolute temperature and obtained very nearly straight lines. These lines are represented very closely by an equation developed by Antoine[25] of the form $\log P = A + \frac{B}{T+C}$ where

[23] Pareau, *Pogg. Ann.*, **1**, 39 (1877).

[24] Baxter and Lansing, THIS JOURNAL, **42**, 419 (1920).

[25] Antoine, *Compt. rend.*, **110**, 632 (1890).

A, B and C are constants. The values for log p and $1/T$ have been calculated from the experimental values given in Tables II and III, and were then used in plotting lines, in the same manner as was done by Baxter and Lansing[24] for their vapor-pressure data. They are shown in Fig. 6. These points, both for the hydrates and saturated solutions, fall within

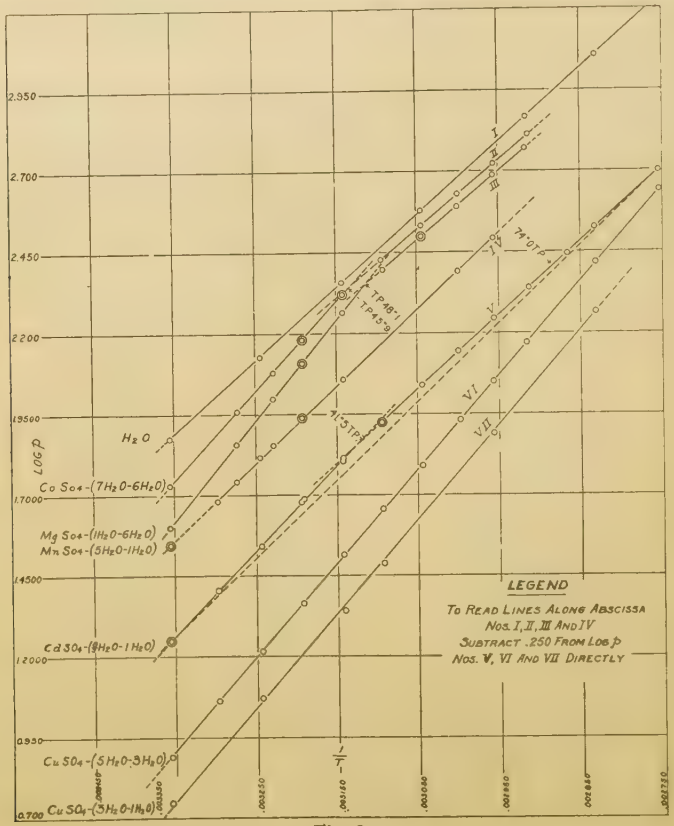

Fig. 6.

the limits of experimental error on straight lines. This is not altogether unexpected for if the equation, $Q = RT^2 \frac{\mathrm{d}\, ln\, p}{\mathrm{d}\, T}$ is integrated, it reduces to the following form, $\frac{1}{T} = \frac{R}{Q} ln\, p + I$, where I is the integration constant.

If, now, Q is constant, then R/Q is a constant and, therefore, the slope of a straight line.

The results shown on these lines are especially striking. The transition points are very definitely located by the intersection of the straight lines. They intersect, in the case of the $MgSO_4.7H_2O$–$6H_2O$, Line III, at a point corresponding to 48.4° and in the case of $CoSO_4.7H_2O$–$6H_2O$, Line II, at 45.9°. These points agree very closely with those indicated on the vapor pressure curves in Fig. 4.

The case of $CdSO_4.8/3H_2O$–$1H_2O$, Line V, gives a very definite indication of a transition point at 41.5°. This seems quite likely for several reasons. If one refers to the vapor-pressure Curve III, Fig. 4, it will be noted that there is a peculiar flattening in its shape about this point. A reference to the solubility diagram Fig. 5, shows that the solubility begins to change more rapidly around this point. The change in Q is as great from 25° to 45° as from 45° to 90°. It is also a well-known fact that in preparing cadmium sulfate for the standard Clark and Weston cell the crystals must be prepared by slow evaporation at low temperatures. While little is known of the nature of the transition, it is possible that it is a molecular rearrangement resulting in a different crystal form.

The point at 74.0°, described by Mylias and Funk,[22] is not shown by any indication of an intersection of lines. It is possible that at the higher pressures, since a small change in log p represents a considerable change in pressure, the irregularity in the normal shape of a curve below and above the transition point, as shown around 74° in the vapor-pressure curve of cadmium sulfate, may not be given definitely by logarithmic expressions. In such a case the two straight lines above and below the transition point may be so nearly similar in direction that the possibility of a sharp intersection is eliminated.

Summary

A thermostat has been assembled for very accurate control of temperatures between 25° and 100°.

The static method has been employed for measuring vapor pressures of hydrates, and a Bremer-Frowein tensimeter, of special design, and manipulation to eliminate the usual errors, have been described.

Equilibrium has been reached from higher and lower pressures simultaneously for each point investigated.

The vapor pressures for $CuSO_4.5H_2O$, $CuSO_4.3H_2O$, $CdSO_4.8/3H_2O$, $CoSO_4.7H_2O$, $MgSO_4.7H_2O$, and $MnSO_4.5H_2O$ crystals, and for the saturated solutions of some of these at various temperatures between 25° and 90°, have been determined.

Certain new transition points have been located, for $CoSO_4.7H_2O$ at 45.1° and for $CdSO_4.8/3H_2O$ at 41.5°.

The transition point for $MgSO_4.7H_2O$–$6H_2O$, previously found by Van der Heide to lie between 48.0° and 48.5°, has been located at 48.4°.

It has been shown that the value of Q usually changes most abruptly at the transition point and that it is nearly constant so long as the same phases are present. On account of this fact most transition points are readily located by the intersection of the lines drawn through the points determined by the log p and $1/T$ relation.

VITA

Eric Randolph Jette was born in Lancaster, Penna., September 30, 1897. His primary and intermediate education was received in the public schools of that city. In 1914, he entered Franklin and Marshall College as a special student in chemistry and later changed to the regular science course. He received the degree of Bachelor of Science in June 1918. From this time until January 1919, he was with the Chemical Warfare Service, stationed at the American University, Washington, D. C. He was then employed by Arthur D. Little, Inc., Cambridge, Mass., until September 1919, when he entered Columbia University as a graduate student. He received the degree of Master of Arts in June 1920. During the last three years, he has been an Assistant in the Department of Chemistry of Columbia University.